

Plastics — a new world of
man-made materials. This
photograph shows the
manufacture of PVC piping.
The piping, as it is 'extruded'
out of the machine, is cooled
with water.
I C I Plastics Division



part one what are plastics?

Most people know something about plastics because these materials are being used more and more to make many of the things we see and use. Look around in your own home or in the local hardware store and you will see many articles made from plastics: dishes, tableware, electric light switches, wash-basins, floor coverings and curtains, and bottles and containers of all shapes and sizes. Plastics are the new materials of the twentieth century; unlike wood, animal and vegetable fibres, metals and minerals, they are made by man. Even more extraordinary, they can take the place of all these conventional materials. Like an actor who can play many different parts, they are versatile; a teacup can now be made of one kind of plastic instead of china clay; even parts of aircraft engines have been made of certain plastics instead of metals. In the last thirty years a great new industry has grown up.

Although plastics are now commonplace, many people do not know what they are or how to distinguish one from another. Often it is thought that plastics are just one material called 'plastic', but this is quite wrong. The plastics are really a group of materials and their properties vary greatly. Some are soft and flexible; others are hard and can be worked as if they were wood or metal. Some are especially useful because they resist acids and other chemicals. Some are important because fibres can be made from them to be used in textile manufacturing.

Plastics are usually solid at ordinary temperatures, but at some stage in their manufacture are made capable of being easily shaped, or plastic. This is the origin of the name 'plastics'. The shaping of plastics materials into useful articles is usually done by applying heat, or pressure, or both.

The characteristic properties of all plastics arise from the great size of their molecules. The molecules of plastics are



Plastics can be shaped into useful articles – usually by applying heat or pressure or both. This is a flowerpot holder made of polypropylene being taken from the mould. *Shell Chemical Company*

very much larger than the molecules of ordinary chemical substances. The molecules of water, for example, are formed of 3 atoms, those of sulphuric acid 7 atoms; and even those of ordinary sugar (sucrose), which has the chemical formula $C_{12}H_{22}O_{11}$, contain only 45 atoms. The molecules of plastics, by contrast, are made up of about 1,000 to 100,000 atoms - a quite different scale of molecular size.



The most characteristic property of plastics is their large molecules. Whereas a sulphuric acid molecule contains only 7 atoms, a Polythene molecule (shown here) may contain up to about 60,000 atoms.

Plastics are made by man. A few are made by modifying natural substances, such as cellulose, which already have large molecules. Most of them are made by the chemical process of building up the large molecules from simple chemical substances. With a few exceptions, plastics are compounds of the element carbon combined with one or more of five other elements: hydrogen, oxygen, nitrogen, chlorine, and fluorine.

The group of substances with very large molecules to which plastics belong are called *polymers*. The word polymer derives from two Greek words meaning many units, and is an apt description of the large molecules which are formed by the linking together of smaller, often identical, molecular units. There are many different types of polymers. Some occur in nature - for example, proteins, starch, wool, silk, cotton (cellulose), and rubber. Others are man-made, and, as well as the plastics, include synthetic fibres and synthetic rubbers. To understand plastics we must take a close look at the chemistry of polymers.

part two how polymers are made



The polymer chemist applies his knowledge of the rearrangement of atoms and the breaking down and building up of molecules to the study of very large molecules called macromolecules. How is it possible to make these very large molecules artificially?

Some polymers result from the complex chemical processes which take place within the animal body or the living plant. Only a few of these natural polymers can be converted into plastics. But it was from the study of natural polymers such as rubber that the idea originated of making large molecules by linking small ones together.

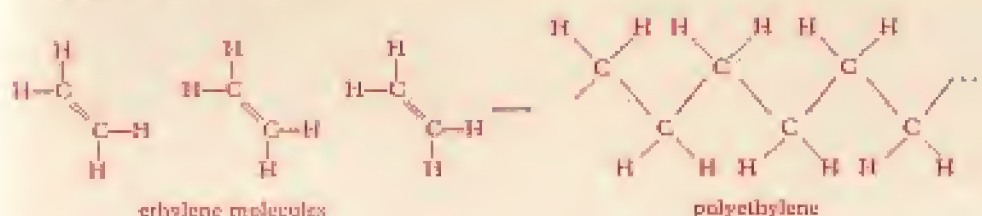
In the plastics industry, there are two chief methods of making large molecules. The object is to use a chemical reaction, called polymerization, to make a large number of small molecules, called the *monomer*, link together to form a large one. The processes for Polythene and nylon exemplify respectively the two different methods.

Polyethylene, or simply Polythene, is a white waxy solid obtained by polymerizing ethylene gas (C_2H_4). This gas is one of the simplest hydrocarbons and is present in the products obtained from the cracking of petroleum (see the Background Book, *Petroleum*).

When heated at $100-300^\circ C$ under pressures of several thousand atmospheres, the molecules of ethylene gas join to

Manufacturing Polythene—
strands of polymer leaving the
cooling bath. Subsequently the
strands are cut up into small
granules for processing into
finished articles.
Shell

Linking together of ethylene molecules to form Polythene.



form long-chain molecules. As in many polymerization reactions, the presence of a small amount of catalyst makes the reaction very much faster.

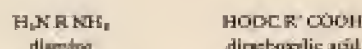
The chemist represents the polymerization of ethylene as above. About 1,000 or even 10,000 molecules may link together to form a long-chain molecule.

The idea that very long molecules could result from the chemical linking of many identical small molecules, a process described as *addition polymerization*, was first suggested by the German chemist Hermann Staudinger, for many years professor of chemistry in the University of Freiburg. He began his work on large molecules about 1922 and was the first to use the term 'macromolecules'. He was the founder of polymer chemistry.

Many of the most important industrial plastics - for example, PVC and Perspex, as well as Polythene - are made from simple chemical substances by addition polymerization. The simple substances that can polymerize in this way have one property in common: there is a double-bond between two carbon atoms; these are called *unsaturated molecules*. This then is the first method of making large molecules.

In the second method small molecules that have a mutually reactive group at each end are linked together, as in the reaction for making nylon. This was discovered by the American chemist W. H. Carothers, another famous pioneer of polymer chemistry. His method depended on the reaction of organic bases (amines) with organic acids. Amines contain the reactive amine group —NH_2 and organic acids contain the reactive carboxyl group —COOH . When a mixture of an amine and an organic acid is heated, the two groups react: water is split off and amine and acid combine to form a larger molecule called an amide.

The key to Carothers's discovery was that he used reactants each of which contained two reactive groups - a diamine and a dicarboxylic acid. These can be represented by the general formulae:



where R and R' are shorthand symbols for the hydrocarbon part of the molecule between the reactive groups.

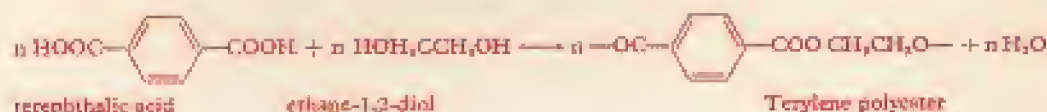
When a mixture of these two reactants is heated, they combine in the normal way, as follows:



The interesting point here is that the product still contains two reactive groups - an amino group at one end and a carboxyl group at the other. Thus the first product can react further - with more acid at one end and with more amine at the other. When this happens, the product still has reactive groups at each end and can therefore continue reacting. The reaction goes on and on. The chain formed gets longer and longer. Eventually a very extended long-chain molecule results, called, in this example, a *polyamide*. It contains a large number of the chemical units $\text{—HN R NH CO R' CO—}$ all joined end to end.

Ordinarily nylon is the polyamide made by starting with hexamethylene diamine ($\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$) and adipic acid ($\text{HOOC}(\text{CH}_2)_4\text{COOH}$). It is often called nylon 66, which is a short way of showing that the diamine and the diacid used to make it each contain six carbon atoms in the molecules. Nylon 66 was the most important of several polyamides dis-

Linking together of terephthalic acid and ethane-1,2-diol molecules to form Terylene.



Taking a sample of nylon polymer as it is being discharged into storage bins.
British Nylon Spinners

covered by Carothers during his researches which began in 1928. He died nine years later at the age of forty-one, but not before it was seen that nylon was a commercial success. As a yarn for making stockings it entered the American market in 1940. Shortly afterwards, because of its toughness, nylon also began to be used by the plastics industry.

The reaction of two molecules to give a larger molecule, with the splitting off of a small molecule (usually water), is called a *condensation reaction*. The use of this kind of reaction to build up polymers (as in the nylon process) is referred to as *polycondensation*. A number of plastics and synthetic fibres are made in this way. Starting, for example, with ethane-1,2-diol, (also known as ethylene glycol, used by the motorist as an anti-freeze agent for his radiator) and terephthalic acid, the polymer obtained is a polyester called polyethylene terephthalate – better known by its commercial name, Terylene.

As you can see from the above equation, the large Terylene molecules are built up in a way similar to the nylon molecules – although here carboxyl groups are reacting with hydroxyl groups (–OH) instead of amines.

Terylene was discovered in Britain in 1941 by Whinfield and Dickson and is now produced on a very large scale, chiefly for use as a fibre.

This distinction between a fibre and a plastic may be confusing. Many synthetic fibres – for example, nylon, Terylene, and Orlon – are made from plastics, but are specially processed to form threads. From the threads fabrics are made which have many of the properties of the polymer and also properties due to their fibre structure such as strength, resistance to creases, or the ability to dry quickly.

part three the structure of polymers

We have pictured polymer molecules as being made up of very long chains of simple chemical units, usually 1,000 or more of them in an actual sample. If we could take a photograph of the polymer, the picture might look like a tangled ball of many long separate pieces of string. To get a more realistic picture we would have to use a motion camera, because the molecules of a polymer, like all chemical molecules, are in a state of motion. The molecular chains possess kinetic energy, and are vibrating and rotating and sliding over one another, rather like a lot of live eels in a bucket.

In polymers the molecular movement tends to be hindered by the entanglement of the long chains with one another. But there is also another restraining influence on the movement of the molecules, from the intermolecular attractive forces. These forces are much weaker than the chemical forces which bind atoms together to form molecules, and they are really effective only when the molecules are very close together. For example, it is because of these cohesive forces between molecules that, under appropriate conditions, gases condense to liquids and liquids change to solids. The existence of inter-



a. Random arrangement of molecular chains of different lengths with the chains continuously coiling and uncoiling. The intermolecular forces are weak and the polymers, which are soft and flexible, are classified as rubbers.



c. Cross-linking between the chains creates, in effect, a single giant molecule - as in thermosetting plastics such as Bakelite.



b. Forces between the chains are stronger and the chains less flexible so give an amorphous structure typical of many thermoplastics.



d. Several chains lie parallel to one another for all or part of their length to produce a close-packed orderly arrangement - as occurs in a number of thermoplastics. These regions of order are described as being crystalline, and the intermolecular forces between the chains are much stronger.

molecular forces of attraction in long-chain molecules is one of the important factors that influence the properties of polymer materials.

Thermoplastics – When a polymer like Polythene is heated, the molecules gain energy and move about more vigorously. The chains therefore become further separated and the inter-molecular attractive forces are weakened. As a result the Polythene becomes softer and more flexible, and on further heating turns into viscous liquid. When the Polythene is cooled, the molecular chains come close together again and attract one another more. The material solidifies and becomes stronger and stiffer.

With polymers like Polythene made up of long-chain molecules, the process of softening on heating and hardening on cooling can be repeated almost indefinitely (provided that the polymer is not heated so strongly that it decomposes). Plastics which have this property are known as *thermoplastics*. Other examples of thermoplastics are PVC and nylon.

Amorphous and crystalline structures – A closer study of the



e Stretching of crystalline polymers results in further alignment of the molecular chains and increased strength. Nylon and Terylene filaments are stretched to convert them into textile fibres.



f In some polymers, the molecular chains are branched and the branches may crystallize among themselves.

internal make-up of Polythene and of other long-chain polymers shows that the arrangement of the molecules is not always completely disordered and random. It is found that in some samples of Polythene, for example, several chains or parts of chains tend to run parallel to one another for all or part of their length, giving a more orderly or closely packed assembly. These regions of orderly alignment of the chains are described as being *crystalline*, in contrast to the regions of disorder which are called *amorphous*. In the crystalline regions the attractive forces between the molecules are greater because the chains lie closer together over a longer distance. Therefore the molecules cannot move as freely over one another and the mechanical strength of the material is greater.

The degree of orderliness in the molecular structure of polymers provides a basis for their broad classification into the three main groups – rubbers, fibre-forming polymers, and amorphous resins. When the intermolecular forces are weak the polymers tend to be completely amorphous and the molecular chains slide easily over one another. Such polymers are soft, flexible, and easily stretched; they are classified as rubbers. Polymers in which the forces are strong have a high degree of crystallinity and are particularly suitable for making fibres. Thermoplastics come somewhere in between, and many of them are partly amorphous and partly crystalline.

The distinction between the three groups is not a hard and fast one. Whether nylon is called a fibre or a plastic depends on what it is used for. Sometimes the degree of crystallinity of a polymer can be partially controlled, and in this way the material can be made specially suitable for a particular use.

Because a knowledge of molecular structure helps to explain the properties of polymers, the study of this subject is of great importance to the industries making rubbers, fibres, and plastics. Many techniques are now available for increasing this knowledge, such as X-ray spectroscopy, electron microscopy, light-scattering, and measurements of viscosities of polymer solutions.

Thermosetting plastics – Some plastics behave quite differently from the thermoplastics when they are heated. A good example is the material commonly known as Bakelite. This is really a trade name for a type of plastic made by the chemical condensation of phenol (C_6H_5OH) and formaldehyde ($HCHO$). It was by causing these two chemicals to react together that the

first fully synthetic plastics were made over fifty years ago by the Belgian chemist Leo Baekeland. The word Bakelite is derived from his name. Similar products with different trade names are now made by many firms in the plastics industry.

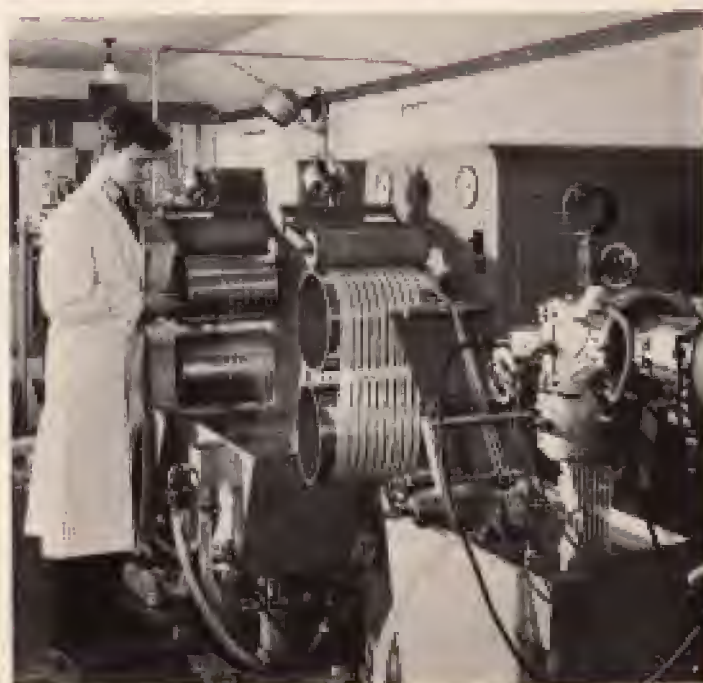
When a large number of molecules of phenol and formaldehyde are heated together under the right conditions, with a suitable catalyst, they undergo a condensation reaction to form polymeric chains similar to those in thermoplastics.

The product is separated as a brownish powder which, when mixed with other ingredients, is known as PF moulding powder, PF being the initial letters of phenol formaldehyde. (Several plastics are commonly known by their initial letters.) PF powder is used to make shaped articles by putting it into a moulding press and subjecting it to further heat and pressure for a short time; the powder is changed to a hard glossy solid which takes up the shape of the mould. Unlike thermoplastic materials the PF plastic cannot be softened again by heating, but remains a hard infusible solid. Plastics like this, which can be softened only once during the moulding process, are said to be thermo-setting.

The reason why plastics of this kind 'set' and become hard when heated is because chemical links are formed between the polymer chains at various points along their length. This process, known as *cross-linking*, firmly binds the chains to one another throughout the mass of the material. The result is that instead of an assembly of separate long chains, the polymer consists of a three-dimensional network in which each original chain molecule is chemically linked with all the others. The whole mass of the polymer is, in effect, one enormous molecule. We could almost think of the casing of one of the older type of telephone receivers, which were made of a PF plastic, as a single visible giant molecule.

A chemical laboratory where research is carried out into the synthesis and properties of plastics.
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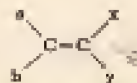
Experimenting with high density Polythene filament. The filament is being extruded from the equipment on the right.
Shell Chemical Company



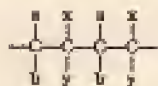
Many other kinds of thermosetting plastics are now produced by the industry. Some of the more common ones are made, like PF, by condensing formaldehyde with another chemical. Two plastics of this type are urea-formaldehyde and melamine-formaldehyde. They have the advantage over the phenol-formaldehyde materials of being light in colour. They can therefore be pigmented to give decorative pastel shades for such things as tableware, electric fittings and radio cabinets.

Molecular manipulation—In the early days of polymer chemistry people tried to find ways in which molecules could be made to link together. Their work led to the two main methods already described—addition polymerization and condensation polymerization. The properties of the resultant polymers were then examined to see whether the polymers might be useful. Nowadays, this hit-and-miss approach has been largely superseded. In a methodical process the monomers are chosen beforehand to give the polymers the kind of properties, strength, density, softening point etc, that are wanted. This new confidence is one of the most exciting developments in present-day chemistry. Its success depends on an understanding of structure.

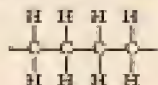
Molecules which undergo addition reactions have the general formula:



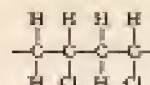
The molecules polymerize to give the following kind of structure:



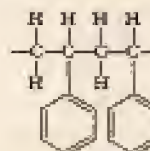
The carbon chain $-C-C-C-C-$ is common to all addition polymers. It is the atoms (or groups) a, b, x, and y which distinguish the addition polymers and which confer their different properties on them. If a, b, x, and y are hydrogen atoms, the polymer is Polythene



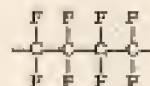
If a, b, and x are hydrogen atoms and y is a chlorine atom, the polymer is PVC.



If a, b, and x are hydrogen atoms and y is a benzene ring, the polymer is polystyrene



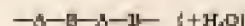
If a, b, x, and y are fluorine atoms, the polymer is polytetrafluoroethylene



By carefully selecting a, b, x, and y, the chemist can make a polymer with the kind of properties that he wants.

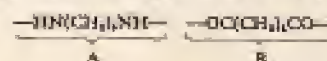
Many molecules which will undergo polycondensation reactions have the general formula $HO-A-OH$ and $H-B-H$ or, occasionally, $H-A-OH$ in which case the substance will polymerize with itself.

The molecules polymerize to give the following kind of structure:

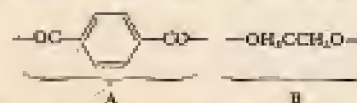


Here it is the groups A and B in the chain (as well as any attachments to these groups) which distinguish the condensation polymers and which confer their different properties on them.

If A and B are the condensation products of hexamethylene diamine and adipic acid, the polymer is nylon



If A and B are the condensation products of terephthalic acid and ethane-1,2-diol, the polymer is Terylene



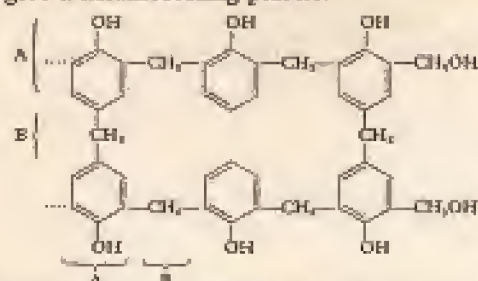
If A and B are the condensation products of phenol and



Series of photographs showing the experiment in which high density Polythene was made for the first time. The experiment was carried out by Professor Karl Ziegler, in 1953, at the Max Planck Institute at Mülheim Ruhr, Germany, and depended on the use of organo-metallic catalysts, which Ziegler had discovered. The series shows ethylene at 1 atmosphere pressure being bubbled through an organo-metallic catalyst with the formation of high density Polythene at over 100 grams an hour. Previously, all Polythene had been made by a high pressure method, and the product had a lower density. Nowadays, large tonnages of high density Polythene are being manufactured too.



formaldehyde, the polymer is Bakelite and here cross-linking occurs to give a thermosetting plastic.



By carefully selecting A and B, the chemist can make a polymer with the kind of properties that he wants. He can vary the properties in the following ways:

By controlling the length of the polymer chains and therefore the softening point of the polymer.

By untangling the twisted molecular chains and bringing them into a state of alignment (usually by stretching the polymer) and thereby increasing the intermolecular forces. This process is especially important in the production of fibres.

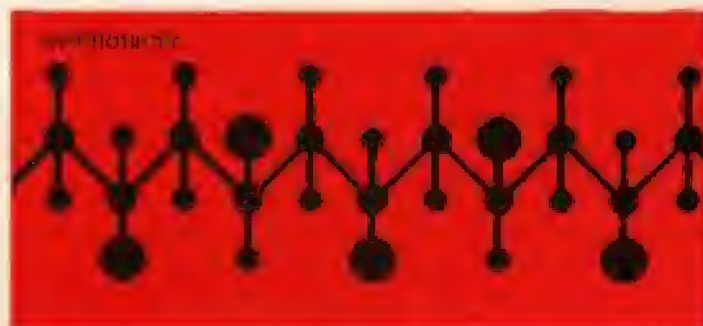
By using special catalysts (developed by Professor Ziegler in Germany) to control the positions of the side groups in the polymer chains and so produce much closer packing of the polymer molecules.

By controlling the molecular weight the softening point of a polymer can be varied. The molecules of a simple substance are all equal in size and they all have the same molecular weight. For example, the molecules of water all have a molecular weight of 18 and the molecules of cane sugar all have a molecular weight of 342. But in a long-chain polymer, although the molecules all have the same basic structure, they are not all of exactly the same length. During polymerization, chains of varying lengths are produced, so that it is necessary to speak of the 'average' molecular weight of the sample of polymer material. The average molecular weight usually depends on the conditions during polymerization. The higher the average molecular weight, the higher the softening point of the polymer.

In what follows, several different plastics are listed and their various properties are described. These plastics between them illustrate some of the ways in which the modern chemist is able to manipulate molecules.

Basic structures of polypropylene. The difference between the three structures depends upon the orientation of the methyl ($-\text{CH}_3$) groups with respect to the other atoms in the chain; orientation of this kind can have a marked influence upon a polymer's properties. So far attempts to make atactic polypropylene have always resulted in an oil because it has proved

impossible to make the chains sufficiently long. By using suitable organo-metallic catalysts (discovered by Professor Ziegler and developed by Professor Natta in Italy) commercial polypropylene is manufactured with a structure that is about 80 per cent isotactic.



part four

some common uses

Plastics, as we have seen, are a group of substances which can be easily moulded by applying heat and pressure. This is why they are such versatile materials for the mass production of shaped articles of many kinds. As well as their useful mechanical properties – strength, toughness, flexibility and so on – plastics have many other valuable characteristics. Many plastics are very resistant to chemical attack by atmospheric oxygen or by corrosive liquids. There are other plastics which have excellent electrical properties and these are widely used in the electrical industry as insulating materials. Some owe their usefulness to their transparency and optical clarity.

PVC



Polyvinyl chloride – One of the most versatile and cheap plastics is PVC, or polyvinyl chloride. It is made industrially in very large amounts, and for a wide variety of applications. Chemically it is the chief member of the vinyl group of plastics, which are so called because they are made by polymerizing monomers containing the vinyl group $\text{CH}_2 = \text{CH—}$: for example, vinyl chloride ($\text{CH}_2 = \text{CHCl}$) and vinyl acetate ($\text{CH}_2 = \text{CHCOOCH}_3$).

PVC is first obtained as a fine white powder which can be processed to give products ranging from soft rubbery materials to hard rigid sheet. Before processing, the PVC is mixed with a small amount of a substance called a *heat stabilizer*; this reduces the tendency of the polymer to decompose if it is overheated during the processing operations.

Depending on what the PVC is to be used for, other ingredients are mixed in with it, and this stage of the processing (which requires some heating) is called *compounding*. For example, to make the PVC more flexible and rubbery, a substance called a *plasticizer* is mixed with it. Plasticizers are usually high-boiling liquids with molecules which are small compared with those of the polymer. The small molecules can go in between the polymer molecules. Thus the polymer chains are pushed apart, they slide more easily over one another, and the material becomes softer. Other ingredients can be added at the compounding stage, for example pigments if a coloured product is wanted.

A large amount of PVC is used in the soft plasticized form as an insulating covering for electric cable and wiring. Soft PVC is also used to make flexible sheet or film by squeezing it through rollers in a machine called a *calender*. Plastic mackintoshes are usually made of PVC sheet.

When mixed cold with larger proportions of plasticizer,

PVC can be made in the form of a paste which can be spread on cloth. After heating, the plastic coating becomes tough and flexible, and the resulting fabric looks like leather. This fabric, known as leathercloth, is often used to cover motor car seats and furniture and to make handbags and suitcase coverings.

There are many important uses of PVC in its hard, unplasticized form. It is used to make long-playing gramophone records, lighting fittings, refrigerator linings, and many other things. Also rigid PVC sheet is being increasingly used in the building industry for roofing, pipes, and guttering.



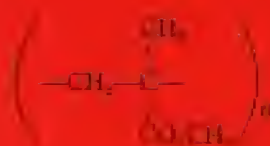
Plastics are very useful materials for electrical insulation. These cables are covered with PVC, one of the most versatile of all plastics. Polythene is also extensively used for electrical insulation.

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The fabric base of leathercloth being coated with PVC which has been softened with large quantities of plasticizer. Leathercloth is used for car upholstery and for making such things as handbags and briefcases.

Sheet

Polymethyl Methacrylate



Acrylics—Acrylic plastics are probably familiar to everyone in the form of a transparent sheet commonly known by its trade name, Perspex. There are several types of acrylic plastics, which differ in their physical form and have different uses. They are called acrylics because the monomer used to make them is a derivative of acrylic acid. This monomer, methyl methacrylate, is a color-clear liquid with a sweetish smell, and it polymerizes to a transparent glasslike solid (polymethyl methacrylate).

It is this glasslike transparency combined with weathering resistance, which determines much of the uses of acrylic plastics. Acrylic sheet is used for many purposes: for windows, especially in aircraft, for display cases, for street-light fixings and for bowls, vases and bathes.

Polymethyl methacrylate can also be moulded in an injection moulding machine. In this form of moulding, the polymer is fed as a powder into the machine. The thermoplastic material is softened by heating and is then forced by a plunger into a mould where it cools and hardens. For this application, the polymer made by the Perspex process is not suitable because the molecular weight is too high. To under-

stand this, imagine a very short, thick rope (the monomer) being pulled apart by two men (the heat). If the rope is very thick, it will break easily. If it is thin, it will not break so easily. The Perspex process makes a very long rope (the polymer) which is too thick to break apart by two men.

Various grades of Perspex acrylic sheet are available. The most common is the standard Perspex, which is clear and tough. It is used for many purposes.



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find why this is so, see the explanation on page 11 of what is meant by the molecular weight of polymers.

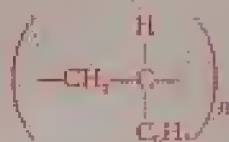
In the injection moulding process, the plastic material must soften rapidly during the short time that it is in the machine. For this type of process, methyl methacrylate is polymerised in a different way from that used for making Perspex sheet. The polymer, of somewhat lower molecular weight, is produced in the form of granules and is referred to as acrylic moulding powder. Chemically it is the same as acrylic sheet and has the same general properties, especially transparency and resistance to the weather.

Acrylic moulding powder is used to make motor car reflectors and lamp housings, lighting fittings, television guard screens, and the coloured Post Office telephones.

A Perspex lamp can be made by the injection moulding method. This lamp consists of a shell of granules of acrylic moulding powder, which is moulded into the shape of a lamp.

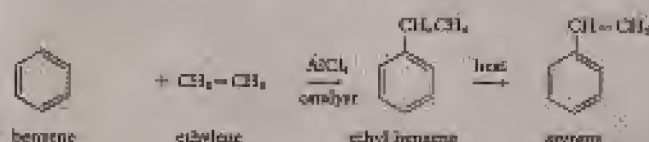


Polystyrene



Polystyrene – Polystyrene is another much-used plastic material, and in terms of world production it is now about the third most important. It is one of the cheapest plastics because it is made from cheap raw materials. Its industrial development, since it was studied by Staudinger about forty years ago, has taken place mainly in Germany and in America.

If benzene is reacted with ethylene and the product (ethyl benzene) is reduced, a liquid called styrene results which is as clear as water. This monomer can be polymerized to give semi-transparent polystyrene granules from which rigid transparent articles can be produced.



Articles made from polystyrene are fairly easily recognized by the tinkling metallic sound they make when they are tapped or dropped on to a hard surface. Polystyrene is used mainly for making packaging materials, refrigerator parts, electrical components, and numerous types of household goods such as egg cups, dishes, and the backs of brushes.

A disadvantage of polystyrene is that it is very brittle. However, it can be toughened by mixing the styrene monomer with other monomers, and polymerizing the mixture to give what are called *co-polymers*. These are polymers which contain more than one chemical unit in the polymer chain, and co-polymerization is yet another of the ways by which the chemist can modify the chemical structure of polymers to alter their properties. In the vinyl group of plastics, several co-polymers of vinyl chloride are made industrially. The

From your work on molecular models, you will probably be familiar with spheres such as these made from expanded polystyrene. The expanded polystyrene has a volume about fifty times as great as the ordinary polystyrene from which it is produced. Its cellular, honeycomb structure is filled with a static blanket of air which makes it an excellent material for heat insulation in buildings.

Shell Chemical Company



The cabinet of this transistor radio is moulded from polystyrene. The case is made from PVC sheet.
Shell Chemical Company

most common co-polymers of styrene are those with butadiene. They form the basis of the most common synthetic rubber known as SBR (styrene butadiene rubber). Another form of polystyrene with which you are probably familiar is expanded polystyrene. The honeycomb structure of this material is filled with a gas and all gases are very good heat insulators. Thus expanded polystyrene is extensively used in the building trade, to keep houses warm and to keep refrigerated stores cold. It also makes a resilient packaging material. You may use it in the chemistry classroom for constructing molecular models.

Polythene



Two polyalkenes — Unsaturated hydrocarbons with one double bond in the molecule are called alkenes, or, to use their old chemical name, olefins. From them, by addition polymerization, it is possible to get polyalkenes. Two polyalkenes are nowadays of industrial importance, polyethylene and polypropylene.

Polythene (polyethylene): The polymerization of ethylene gas to give a waxy solid polymer has already been described. The discovery of polyethylene in 1933 was an accident. It happened in the Winnington laboratories of I.C.I. during a research programme to study the effect of very high pressures on chemical reactions. In one of these experiments involving ethylene, a small amount of an unusual white solid was obtained which proved to be polyethylene. It was found to have interesting properties. It was resistant to chemicals, could be moulded by heat and pressure and was a very good electrical insulator. By 1939 Polythene (as it came to be called) was made on a commercial scale as an insulator for submarine cables, which is still one of its most useful applications.

During the Second World War, all the Polythene made was used for military purposes. Radar equipment owed its development to the fact that Polythene was just the right kind of material to solve the problems of electrical insulation. After the War many other industrial and domestic applications were found for this useful plastics material. Production went up at a rapid rate and, with a world-wide annual production of over two million tons, it is probably the commonest plastics material.

Polythene is normally made in the form of small chips which can be fed into various types of moulds to make such shaped articles as bowls, buckets, watering cans, and bottle-



Many household items are made of plastic materials — polythene. Products are often made from polythene.

A large quantity of polythene chips being produced. These are used to make the various articles and in large quantities for making pipes.

Polypropylene



stoppers. Polythene can also be converted into a flexible film which is tough and waterproof. This film, which is used for wrapping foodstuffs and other products, is the biggest single application of Polythene. Increasing amounts are also being used for making squeeze-bottles and containers of many kinds, and in the manufacture of piping. Polythene pipes have a great advantage over metal pipes because they can be welded quickly and do not burst in frosty weather.

In 1953 Professor Ziegler, working on polymerization problems in Germany, discovered that ethylene could be polymerized at atmospheric pressure by using special organo-metallic catalysts (see photographs on page 11). The solid Polythene made in this way is very similar to that made by the high pressure process, but it is more crystalline, has a more closely packed chain structure and is therefore more dense. This newer material is known as 'low pressure' or 'high density' Polythene. Unlike high pressure Polythene, it does not soften at the temperature of boiling water and is especially useful for making articles that need sterilizing.

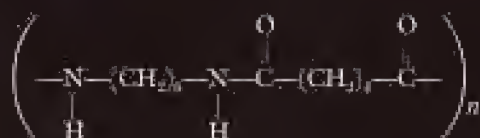
Polypropylene In 1951 Professor Natta in Italy, using catalysts of the type developed by Ziegler, succeeded in polymerizing the next higher member of the family of alkenes — namely propylene ($\text{CH}_2 = \text{CHCH}_3$). Polypropylene is more rigid and heat resistant than polythene, so that it extends still further the range of properties of the polythene plastics.

Polypropylene is used for many types of plastic and is also a major constituent of many plastics. It is used for making many types of plastic, such as pipes, containers, and many other plastic products.

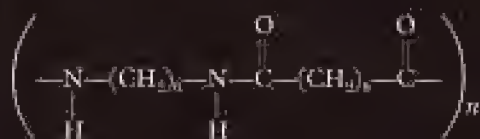


Nylon

Nylon 66



Nylon 610



Nylon—In Part II, the polyamide nylon 66 was given as an example of a polymer made by the method of polycondensation. Actually a number of different polyamides are now made commercially for use as fibres and as plastics, and the term 'nylon' is used as a general name for all these materials. They are distinguished by numbers, which stand for the number of carbon atoms in the diamine and diacid units from which the polymers are built up.

For plastics purposes, two main types of nylon are made in this country. One is nylon 66. The other is nylon 610 (six-ten) which is made from hexamethylene diamine (6 carbon atoms) and sebacic acid (10 carbon atoms). Another type of nylon, developed mainly in Germany, is known as nylon 6. This is made by a polycondensation process in which an amino-acid is condensed with itself. It is possible to do this because an amino-acid has a different reactive group at each end of the molecule—an amino group at one end and a carboxyl group at the other. The amino-acid from which nylon 6 is made is aminocaproic acid ($\text{H}_2\text{N}(\text{CH}_2)_5\text{COOH}$). These three nylons are the most important ones in the plastics industry. Other nylon compositions are made by blending to-

gether the standard nylons, so that it is possible to get nylon products with a varied range of properties.

Nylon 66, the original member of the group, is a tough waxy solid with a high mechanical strength. It is a very useful material for the manufacture of lightweight gear wheels and other machine components. It is also used to make curtain rails and runners, which are durable, non-rusting, and do not need to be lubricated.

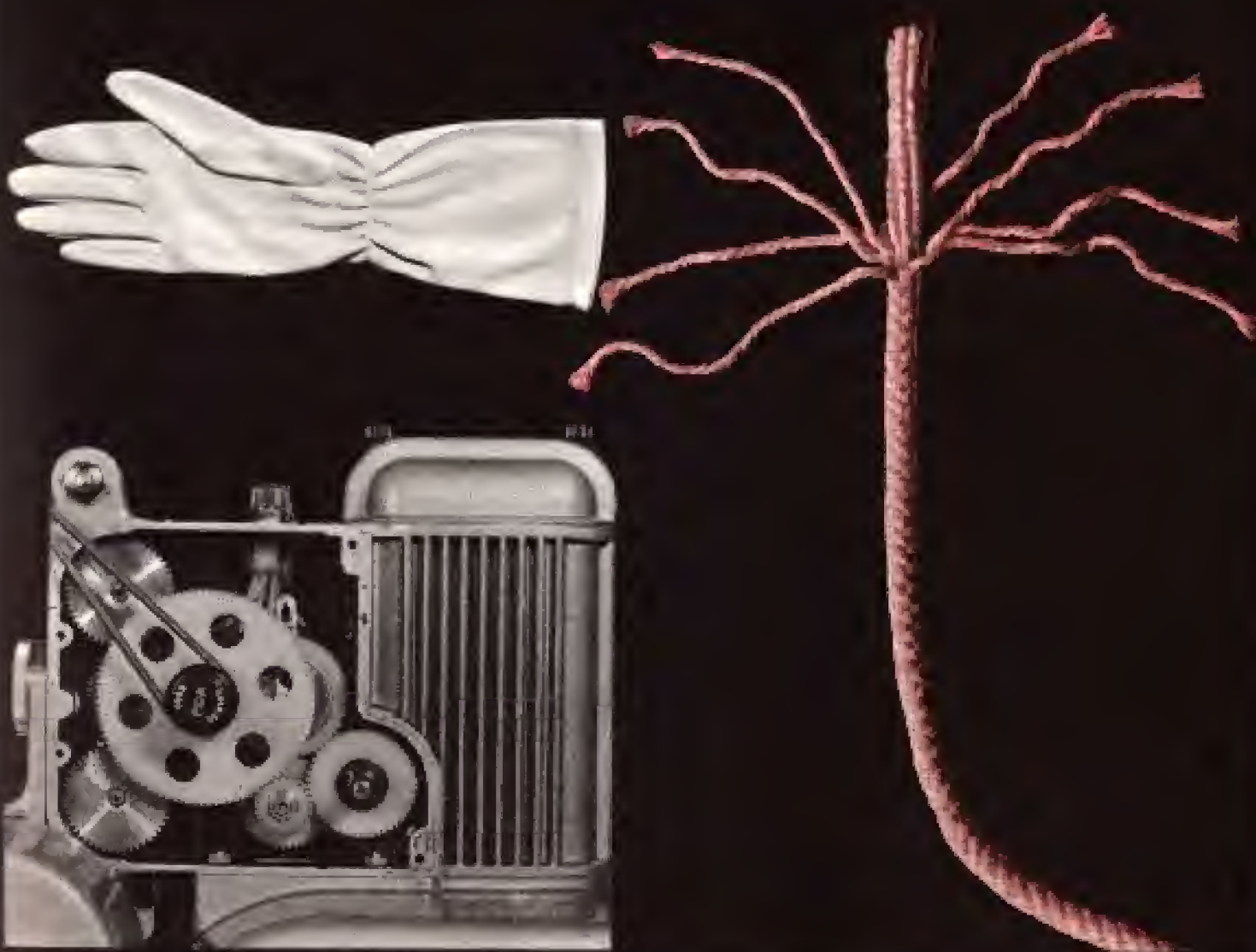
In the form of filaments much thicker than the very fine threads used to make stockings, nylon is woven into cord and ropes which are very strong, durable, and light. Nylon filaments (usually nylon 610) are also used for making bristles for many kinds of brushes.



**Some of the varied uses of
nylon.**

As a plastics material: for gear
wheels and for brush bristles.
I.C.I. Plastics Division

As a textile fibre for clothing;
and for ropes.
British Nylon Spinners



Other plastics

Other plastics – Although the list above mentions most of the commonest plastics, there are many others of importance. One of these is polytetrafluoroethylene (PTFE) which is similar to Polythene except that it has fluorine atoms in place of hydrogen. Because of its extreme inertness, it will resist the attack of the most corrosive acids. Another is polyurethane which is produced as a foam – either a rigid foam, which is used for heat insulation, or a flexible foam, which is used for cushioning. Others are the thermosetting resins which, apart from their extensive use in paints, form the basis of the modern adhesives which are supplied as a tube of resin and a tube of cross-linking agent. Every few years more new plastics come into prominence and nowadays, with a much greater insight into the nature of polymers, the chemist can go about his work of creating new plastics much more methodically.

These cast-iron cooking pots are coated with polytetrafluoroethylene (PTFE) which makes a very slippery surface. They are therefore very easy to wash up.

I.C.I.



Polyurethane is a thermosetting plastic. In the chemical reaction to make the polymer, carbon dioxide is given off, causing the polymer to expand into a foam. In the foreground of the photograph is the mixing head which squirts the reactants for making polyurethane into the tray beneath. The flexible foam shown here is used chiefly as a cushioning material or for backing coats. Rigid foam is used chiefly for heat insulation. *Shell Chemical Company*



part five the plastics industry

The making of plastics materials and their conversion into finished products and usable articles is the work of the plastics industry. The industry is composed of many different kinds of companies. Those that make the polymers are called manufacturers of plastics raw material and they are essentially part of the chemical industry. There are also a large number of fabricators or converters who change the raw materials into finished products by moulding, extruding, and a variety of other processes. The makers of the special plant and equipment used in these processes are also regarded as part of the plastics industry. The industry as a whole is, therefore, a very complex one and overlaps the chemical and engineering industries.

Making the raw materials – The carrying out of polymerization reactions on an industrial scale, which is the job of the manufacturers of plastics raw materials, is a much more complicated business than making small amounts of polymer in the laboratory. Since the properties of plastics depend very much on their chemical structure, plastics materials must be made of a constant and reproducible composition.

Industrial polymerization processes require a great variety of plant and equipment. For example, the making of Polythene by the original process has to be done in plant able to withstand very high pressures of 1,000 atmospheres or more. In a PVC plant, the vinyl chloride monomer is polymerized in pressure vessels, called autoclaves, in which the volatile monomer, mixed with water, has to be stirred continually during the reaction. In the manufacture of clear acrylic sheet, the liquid monomer, containing a small amount of catalyst, is run into glass moulds at ordinary pressure and polymerized by heating the moulds in large ovens under carefully con-

trolled conditions. These few examples of the kind of plant used in making plastics show that this section of the industry involves not only chemical processing on a large scale but also much engineering and technological skill.

Many manufacturers of plastics raw materials in this country and abroad belong to large chemical companies. These companies also make many of the monomers and organic chemicals which are used to make polymers and which are derived very largely from the cracking of petroleum (see the Background Book, *Petroleum*).

Making the finished goods – The products of the plastics raw materials manufacturers are sent to the fabricators in a variety of forms. They may be powders, small chips or granules, and occasionally viscous liquids. Some plastics materials are made in such semi-finished forms as sheet, film, rod, or tubing. Many different processes of plastics technology are used by the fabricating and converting section of the industry to change these materials into usable products.

The usual way of making shaped articles from plastics is in some form of heated mould under pressure. The commonest types of moulding processes are compression moulding, injection moulding, blow moulding, and vacuum forming. Plastics can also be extruded through shaped holes to produce such equipment as piping. Some of these processes are shown in the illustrations. The machinery required may cost several thousands of pounds, and the plastics materials, compared, for example, with wood, are expensive. But so efficient are the machines at turning out precisely shaped articles at a very quick rate that articles made from plastics are usually cheaper to buy than similar articles made from other materials.

Chemical plant for the manufacture of polyalkene plastics. As you can see, the equipment is extremely complex and the construction and maintenance calls on the highest skill of both the chemist and engineer.

Shell

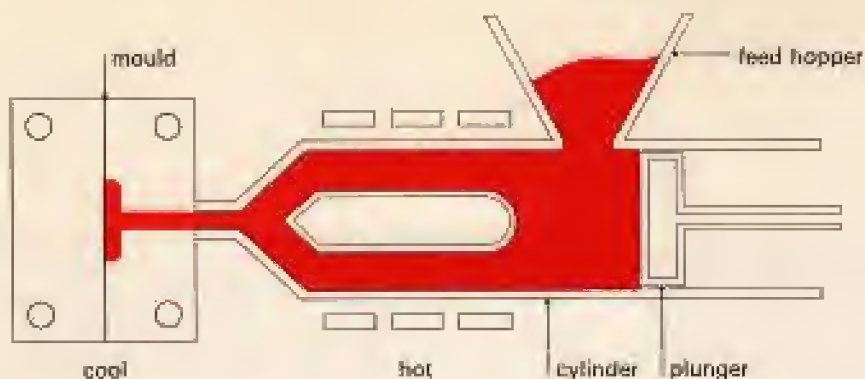


Methods used for making shaped articles from plastic depend on whether the material is thermoplastic or thermosetting. First some methods for thermoplastics:



Plastics come from the raw materials manufacturers in several forms: powder, granules (as shown here), viscous liquids; or sheet, film, rod, or tubing. These materials are converted into useful articles.
Shell Chemical Company





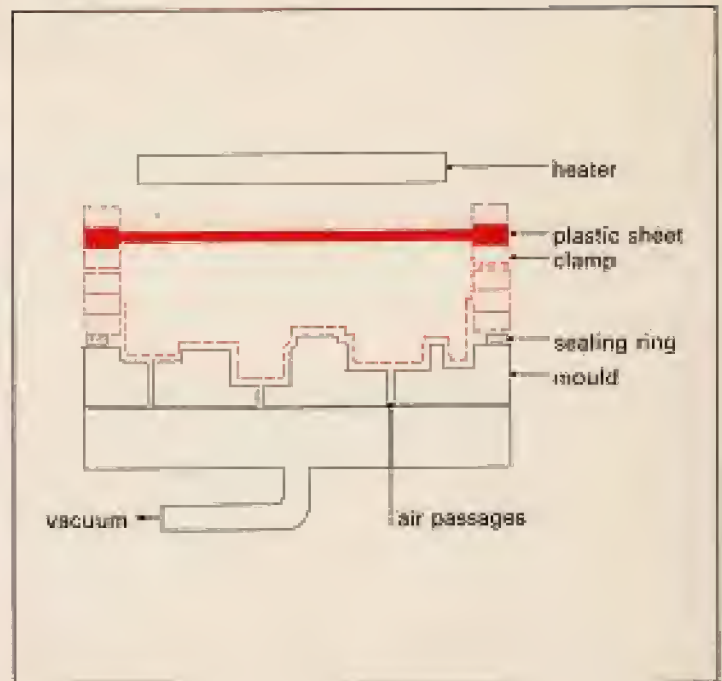
a. Injection moulding — granulated thermoplastic is fed through a hopper into a heated cylinder. The cylinder has a plunger at one end and a hole at the other. The softened thermoplastic is forced by the plunger through the hole into the unheated mould. The thermoplastic cools, the mould opens, and the finished article is ejected.
Shell Chemical Company



cycle of operations used in producing a bottle from an extruded tube

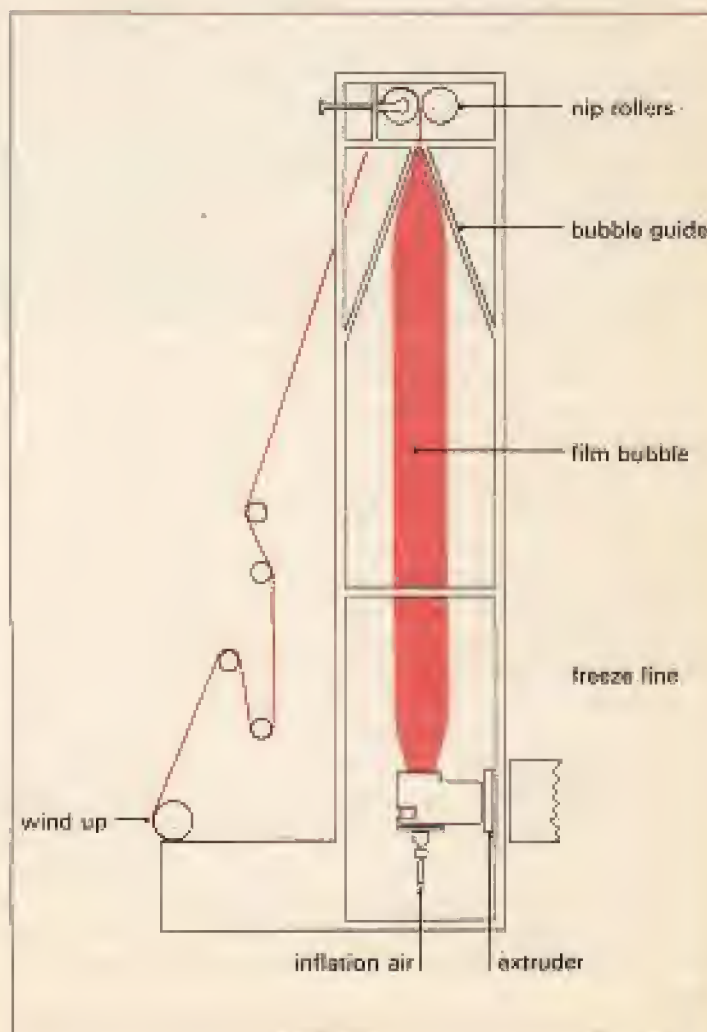
b. Blow moulding — this process is used to produce bottles and other hollow containers with a small opening. A length of softened plastic tube is inserted in the hollow cavity of the vertically split mould. As the mould closes round the tube, it seals off one end. Compressed air, forced in at the other end, blows the tube into shape. The mould opens and the hollow container is ejected.
Shell Chemical Company

c. Vacuum forming — heated plastics sheet is drawn over a mould, a vacuum is created in the space between the sheet and the mould, and the plastics sheet is sucked on to the mould shape; pressure forming is the reverse process.
I.C.I. Plastics Division



d. Extrusion — granulated thermoplastic is fed into a heated cylinder and is continuously moved forward by a revolving screw. Upon reaching the end of the screw the thermoplastic is forced through a hole whose shape determines the resultant shape of the material. Here air is being blown into the extruded material to produce tubular film. The photograph on the inside of

the front cover shows piping being extruded. Shell Chemical Company



Another way of using plastics materials is in the manufacture of what are called reinforced plastics. These are products of high strength made by impregnating such materials as paper, wood, cloth or glass fibre with plastics, and bonding them together by heat and pressure into one solid structure. In *laminated plastics*, for example, the bonded material is in the form of layers of paper, cloth, or some other fabric, and the bonding material is commonly a phenol-formaldehyde or urea-formaldehyde polymer. Laminated plastics are used to make partitions and panels for the building industry, electrical panels and components, table-tops, and other forms of decorative coverings. Many plastics can be made into finished articles using methods similar to those for wood and metal-working.

The growth of the plastics industry - The plastics industry is now regarded as one of the basic industries in the economy of any industrial country. Its products are needed by practically every other industry.

One of the most striking things about the plastics industry has been its rapid rate of growth, especially during the last twenty-five years. The first man-made plastic was produced about a hundred years ago. It was made by Alexander Parkes of Birmingham and he called it Parkesine. It consisted of cellulose nitrate mixed with castor oil and a solvent. A few years later an American called John Hyatt brought out an improved form of cellulose nitrate plasticized with camphor. This plastic became known as celluloid. Neither of these early plastics was completely synthetic. They were chemical modifications of cellulose, a polymer occurring naturally. As mentioned earlier, the first fully synthetic plastic (Bakelite) was made just over fifty years ago.

Until 1939 the plastics industry remained fairly small. Thirty years ago the annual production of all plastics in this country was only about 10,000 tons. Since the war, very many new plastics materials have been made and many new uses have been found for already established products. Production of some of these has expanded very rapidly indeed, and the making of plastics has now become big business.

In Britain nearly 750,000 tons of plastics raw materials were produced in 1963, with a total value of over £170 million.

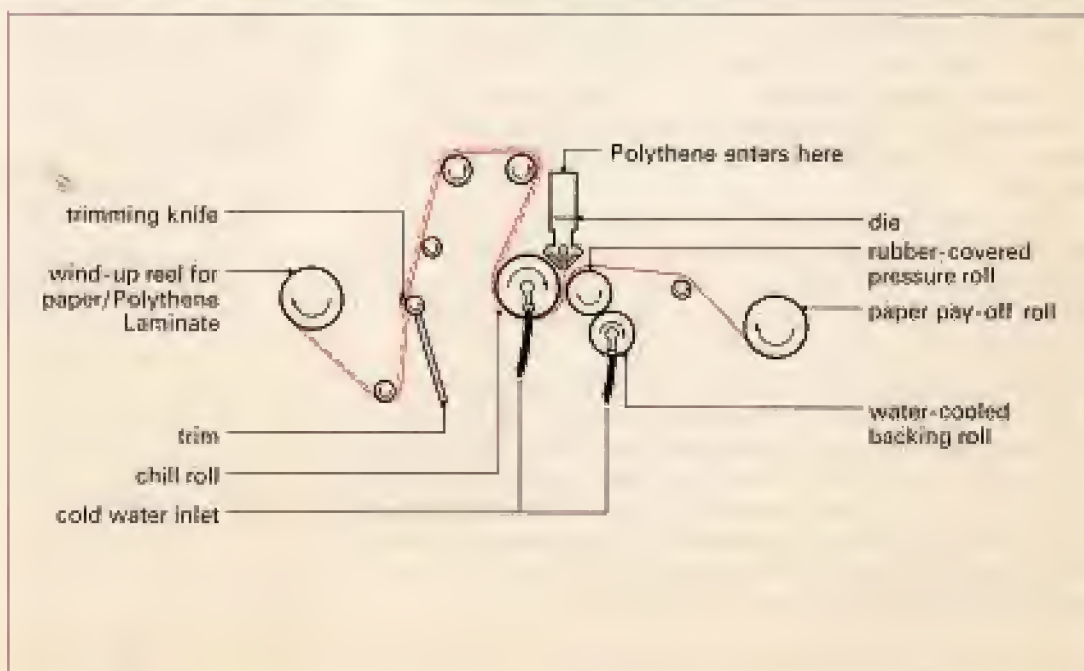
Many other countries have flourishing plastics industries.

Thermosetting plastics.
a. Compression moulding - A two-piece mould is heated with steam and the lower half is filled with a pellet of the thermosetting moulding powder. The pellet softens, the upper half of the mould is compressed on to the lower, and the powder is forced into the mould shape. Cross-linking occurs and the mould opens to eject the finished article. The photograph

shows electrical equipment made of Bakelite being lifted from a compression mould. Bakelite Ltd



Lamination is a processing method that can be used for both thermoplastic and thermosetting plastics. The plastic material can be impregnated on to paper (as shown here) or it can be used (somewhat like glue) to bond layers of glass fibre, chipboard, or cloth.
Bakelite Ltd



A brilliant ball, buttons, curtain ring, and paper knife made from Parkesine, the first plastics material: Parkesine, made by Alexander Parkes just over a hundred years ago, is similar to celluloid.

Crown Copyright. Science Museum



The United Kingdom is at present fourth among the leading producers, after the United States, West Germany, and Japan. After these come Italy and France. This list does not include Russia, who started late in the making of plastics but claims to have made nearly 600,000 tons in 1963.

The total world production of plastics materials in 1963 was probably not far short of ten million tons.

The future of plastics – It seems fairly certain that the rapid growth of the plastics industry will continue for many years to come. New plastics continue to be discovered and new uses found for existing plastics. In some large industries – agriculture, motor car manufacture, and building which already use a large tonnage of plastics – there are many uses to which plastics have yet to be adapted. One motor car may at present use up to 35 lb of plastics, a figure which could certainly be increased.

It has been confidently predicted that by 1970 the production of plastics in Britain will reach well over one million tons a year. By 1980 this figure may well be doubled. A Russian scientist has forecast that in about twenty years the production of plastics may surpass that of steel.

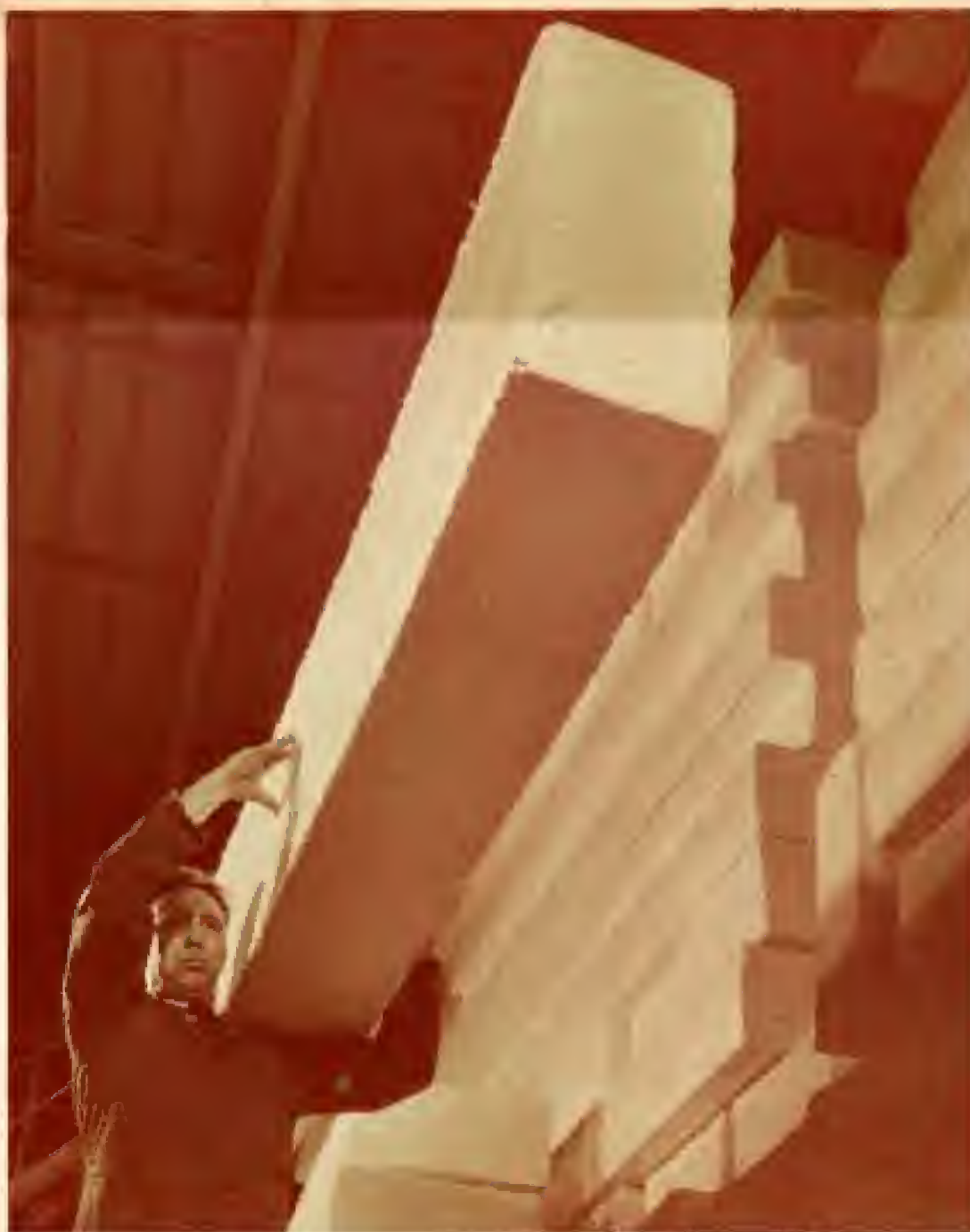
Whatever may be the accuracy of these predictions, it seems certain that more and more applications of plastics will be found as scientists, technologists, manufacturers, architects and builders, and other interested people, explore further the nature and properties of these materials. The search will also continue for materials with improved properties, which will stand up to the more testing requirements of the exploration of space and of nuclear power.

Questions

1. List at least twenty articles in your house that are made from plastics materials. If you can, give the names of the different materials.
2. Outline some of the properties of polymers that distinguish them from other substances.
3. Which plastics materials would you choose to make the following articles, and why?
 - a. Outdoor piping for carrying cold water
 - b. A raincoat
 - c. An ashtray
 - d. A bottle that can be sterilized
 - e. Windows
 - f. A squeeze bottle
 - g. Insulating material for a cold-storage room
 - h. A bottle for containing concentrated acids
 - i. Cheap packaging material
4. What would you expect to be the structure of polymers made from the following monomers:
 - a. Oxalic acid (HOOCCOOH) and ethane-1,2-diol ($\text{HOCH}_2\text{CH}_2\text{OH}$)
 - b. Vinylidene chloride ($\text{CH}_2=\text{CCl}_2$)

Elastics have a big future, especially in such industries as building and motor car manufacturing where there is scope for using very large sheets. These blocks of expanded polystyrene are used chiefly for the heat insulation of buildings.

Shell Chemical Company



Chemistry Background Books

General author: J. H. Oliver. Author of *The Book of Quaternions*

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